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The FTIR Laboratory in Support of the PV Program

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ABSTRACT

The Fourier Transform Infrared Spectroscopy (FTIR) Laboratory supports the Solar Energy Technologies Program through the measurement and characterization of solar energy-related materials and devices. The FTIR technique is a fast, accurate, and reliable method for studying molecular structure and composition. This ability to identify atomic species and their bonding environment is a powerful combination that finds use in many research and development efforts. A brief overview of the technical approach used is contained in Section 2 of this report.

Because of its versatility and accessibility, the FTIR Laboratory is a valuable contributor to the Solar Energy Technologies Program. The laboratory provides support for, and collaborates with, several in-house programs as well as our industry and university partners. By the end of FY 2004, the FTIR Laboratory performed over 1100 measurements on PV-related materials. These contributions resulted in conference and workshop presentations and several peer-reviewed publications. A brief summary of a few of these efforts is contained in Section 3 of this report.

1. Objectives

The FTIR Laboratory has one objective – to support the Solar Energy Technologies Program through the measurement and characterization of solar energy related materials and devices. The specific areas and extent of support are a result of matching the goals of the Multi-Year Technical Plan with the capabilities of the FTIR technique.

2. Technical Approach

The infrared region of the electromagnetic spectrum spans from about 50 to 12,000 cm^{-1} (0.006 to 1.5 eV) and is commensurate with the energy required to excite rotations and vibrations of the chemical bonds between the constituents of a compound. Consequently, this energy range is ideal for characterizing the chemical make-up of materials. NREL utilizes FTIR spectrometers because of their increased signal-to-noise, resolution, accuracy, and reduced measurement time relative to dispersive spectrometers, to perform reflectance and transmittance measurements over this spectral range. These data are then analyzed to provide qualitative and quantitative analysis of the molecular composition of host atoms and impurities in organic and inorganic compounds.

The FTIR Lab also analyzes the absorption of free-charge carriers within a metal or semiconductor. In this case, the frequency dependence of the absorption process is a function of several important transport parameters including the density of carriers and their effective mass. This approach is proving very useful in the development of new transparent conducting oxides (TCO).

The advantages of the FT technique are also utilized in Fourier-transform Raman spectroscopy and Fourier-transform Photoluminescence spectroscopy. Raman spectroscopy reveals information on the chemical bonds similar to that discussed above for the FTIR technique. Photoluminescence spectroscopy analyzes the radiation emitted from electronic transitions and provides information on the bandgap and electron defect levels.

3. Results and Accomplishments

3.1 Crystalline silicon

Because of its rapid, nondestructive nature, industry and university partners use FTIR spectroscopy to evaluate crystalline silicon and related materials. Using FTIR transmittance analysis, impurities in highly resistive silicon can be detected and quantified. Interstitial oxygen and substitutional carbon concentrations are calculated per ASTM methods F 1188-93 and F 1391-93, respectively. In addition, we can determine absorption coefficients of oxygen precipitates, SiNx, and SiCx phases if present. High impurity or precipitate levels usually adversely affect device performance, therefore concentrations must be known for maximizing process control in manufacturing.

FTIR transmittance analysis is also an effective means for studying related materials such as amorphous SiNx deposited on crystalline silicon. In these studies, the FTIR Lab provides timely measurements of N-H and Si-H bonding in silicon nitride coatings. This is often associated with concurrent changes in growth or processing (e.g., before and after a series of annealing steps).

3.2 Amorphous silicon and related alloys

Infrared absorption is routinely used to study the material properties of a-Si:H, µc-Si:H, and a-SiGe:H. Of primary interest is the hydrogen content and how it changes with growth, processing, etc. The hydrogen-related modes are also sensitive to the degree of microcrystallinity and provide a useful measure in characterizing the amorphous-to-microcrystalline transition. Additionally, because films with higher crystalline volume fractions favor increased oxidation, monitoring oxygen-related absorption regions proves to be a valuable exercise in predicting device quality.

As with silicon films, hydrogen content and its bonding configuration are also important in silicon-germanium alloys where increased Ge-H bonding, detectable by FTIR, is found to correlate with higher-quality alloys.

3.3 Transparent conducting oxide films

Transparent conducting oxides are currently employed as a contact layer in several thin-film solar cell technologies. This broad applicability makes the improvement of existing materials and the search for new and better material systems a vital part of the research and development efforts at NREL. In response to increased development efforts, especially in the area of combinatorial growth, the FTIR lab has added large-area reflectance and transmittance infrared mapping capabilities for higher-throughput TCO library characterization. These optical measurements are used to calculate carrier concentration and, hence, conductivity, and can be combined with other measurements to more efficiently optimize material growth parameters.

The development of a p-type TCO is also a high-priority research effort fraught with difficulty and an inadequate understanding of material impurities and their impact on the majority-carrier concentration. This is exemplified by the difficulties in understanding the problems associated with making p-type ZnO through the incorporation of nitrogen as an acceptor. The FTIR Lab shed light on this problem by providing the first experimental evidence of unintentional hydrogen bonding with, and passivating, the nitrogen acceptor states in polycrystalline ZnO:N.

3.4 ZnS buffer layers for $CuInGaSe_2$-based devices

Chemical bath deposited (CBD) CdS is currently the dominant window layer used in $CuInGaSe_2$-based polycrystalline thin-film devices. The search for an improved and Cd-free replacement is of interest to the PV community. Recently, a single-layer CBD ZnS(O,OH) layer substituted for the CBD CdS has demonstrated 18.5% device efficiency. The higher bandgap of ZnS (~3.8 eV) compared to CdS (~2.4 eV) is an added advantage, which should improve the device efficiency by eliminating absorption loss. Ultimately, the CIS community is expecting to achieve a 20%-efficient CIGS-based device using CBD ZnS(O,OH).

The FTIR Lab contributed to this effort through an analysis of the deposited films. This effort revealed the presence of several likely impurities, including cyanamide (NCN^{2-}) or thiocyanate (SCN^-), which resulted from the chemical reaction of thiourea and ammonia, as well as carbonate (CO_3^{2-}) impurities. The data also revealed the presence of $Zn(OH)_2$ in the CBD ZnS(O,OH).

4. Conclusions

In FY 2004, the FTIR Laboratory performed over 1100 measurements on PV-related materials. These contributions resulted in conference and workshop presentations and several peer-reviewed publications. Because of its versatility, accessibility, and wide range of applications, the FTIR Laboratory is a valuable contributor to the Solar Energy Technologies Program. These contributions — a few of which are briefly discussed in this report — support collaborations with in-house programs as well as our industry and university partners. The specific areas and extent of support are a result of matching the goals of the Multi-Year Technical Plan with the capabilities of the FTIR technique.

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MAJOR PUBLICATIONS

B. M. Keyes, L. M. Gedvilas, X. Li, and T. J. Coutts, "Infrared spectroscopy of polycrystalline ZnO and ZnO:N thin films," submitted for publication.

Q. Wang, S. Ward, L. Gedvilas, B. Keyes, E. Sanchez, and S. Wang, "Conformal thin-film silicon nitride deposited by hot-wire chemical vapor deposition," *Applied Physics Letters* **84**(3), 338 (2004).

C. Warmsingh, Y. Yoshida, D. W. Readey, C. W. Teplin, J. D. Perkins, P. A. Parilla, L. M. Gedvilas, B. M. Keyes, and D. S. Ginley, "High-mobility transparent conducting Mo-doped In 2O3thin films by pulsed laser deposition," *Journal of Applied Physics* **95**(7), 3831 (2004).

F. Liu, S. Ward, L. Gedvilas, B. Keyes, B. To, and Q. Wang, E. Sanchez and S. Wang, "Amorphous silicon nitride deposited by hot-wire chemical vapor deposition," *Journal of Applied Physics* **96**(5), 2973 (2004).

S. P. Ahrenkiel, M. W. Wanlass, J. J. Carapella, L. M. Gedvilas, B. M. Keyes, R. K. Ahrenkiel, and H. R. Moutinho, "Characterization Survey of $Ga_xIn_{1-x}As/InAs_yP_{1-y}$ Double Heterostructures and $InAs_yP_{1-y}$ Multilayers Grown on InP," *Journal of Electronic Materials* **33**(3), 185 (2004).

R. C. Reedy, J. F. Geisz, A. J. Ptak, B. M. Keyes and W. K. Metzger, "Characterization of light element impurities in gallium-nitride-phosphide by SIMS analysis," *Applied Surface Science* **231-232**, 808 (2004).

J. D. Perkins, C. W. Teplin, M. F. A. M van Hest, J. L. Alleman, X. Li, M. S. Dabney, B. M. Keyes , L. M. Gedvilas, D. S. Ginley, Y. Lin and Y. Lu, "Optical analysis of thin film combinatorial libraries," *Applied Surface Science* **223**, 124 (2004).

C. W. Teplin, M. F. A. M. van Hest, M. Dabney, C. L. Perkins, L. M. Gedvillas, B. To, P. A. Parilla, B. M. Keyes, J. D. Perkins, D. S. Ginley, Yuping Lin and Yiwei Lu, "Combinatorial study of reactively sputtered Cr–Ti–N," *Applied Surface Science* **223**(1-3), 253 (2004).

L. M. Gedvilas and A. H. Mahan, "Identification of Possible Bonding Sites for Post Deposition Oxygen Absorption in Microcrystalline Silicon," *MRS Proceedings*, April 2004.

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